

PATENT APPLICATION

Attorney Docket No. A03092US (15630.141)

TITLE OF THE INVENTION:

5       "Improved Catalyst and Process to Produce Nanocarbon  
Materials in High Yield and at High Selectivity at  
Reduced Reaction Temperatures"

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CROSS-REFERENCE TO RELATED APPLICATIONS

10       None

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT

Not applicable

REFERENCE TO A "MICROFICHE APPENDIX"

15       Not applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

20       The present invention relates to the production of  
Nanocarbon materials. More particularly, the present  
invention relates to an improved catalyst and process to  
produce Nanocarbon materials in high yield and high  
selectivity and at reduced reaction temperatures.

2. General Background of the Invention

25       Nano-structured materials, more particular carbon nano  
structure materials, are gaining importance for various  
commercial applications. Such applications include their  
use to store molecular hydrogen, to serve as catalyst  
supports, as reinforcing components of polymeric  
composites, for use in electromagnetic shielding and for  
30   use in various types of batteries and other energy storage  
devices. Carbon nano-structure materials are generally  
prepared from the decomposition of carbon containing gases  
over selected catalytic metal surfaces at temperatures  
ranging from about 500°C to about 1200°C.

35       For example, carbon nanofibers can be used in lithium

ion batteries, wherein the anode would be comprised of graphitic nanofibers. The graphite sheets are substantially perpendicular or parallel to the longitudinal axis of the carbon nanofiber. Example of such a use can be found in U.S. Patent No. 6,503,660 which is contained in the information disclosure statement submitted herewith. Furthermore U.S. Patent No. 5,879,836 teaches the use of fibrils as a material for the lithium ion battery anode. Fibrils are described as being composed of parallel layers of carbon in the form of a series of concentric tubes disposed about a longitudinal axis rather than as multi-layers of flat graphite sheets.

Furthermore in U.S. Patent No. 6,485,858 the graphite nanofibers possess structures in which the graphite sheets are aligned in the direction either substantially perpendicular or substantially parallel to the fiber axis and designated as platelet and ribbon respectively. In addition, the exposed surfaces of the nanofibers are comprised of at least 95% edge regions in contrast to conventional graphites that are comprised almost entirely of basal plane regions and very little edge sites.

Other references include "Catalytic Growth of Carbon Filaments," which is an article from the Chemical Engineering Department of Auburn University dated 1989, wherein it discusses the formation of filamentous carbon. Another source of information is an article entitled "A Review of Catalytic Grown Carbon Nanofibers," published by the Material Research Society, in 1993. In that article, carbon nanofibers are discussed as being produced in a relatively large scale through a catalytic decomposition of certain hydrocarbons on small metal particles.

In all cases, as was discussed above, synthesizing a pure carbon nanomaterial is challenging. Most of the applications of these materials require pure carbon nanomaterials systems. Therefore, it would be beneficial

to provide a system of producing pure carbon nanomaterials where the carbon system can be synthesized with very high purity (greater than 95%), high crystallinity, selectivity of the carbon morphology, and exceptionally high yield.

5 Furthermore, a custom made catalyst with a particular particle size and high surface area would give a higher selectivity and higher reactivity.

#### BRIEF SUMMARY OF THE INVENTION

10 In the present invention, a carbon nanofiber system is synthesized with very high purity (above 95%), high crystallinity, selectivity of the carbon morphology, and exceptionally high yield. A custom made catalyst with an average single crystal-particle size of  $\leq 10$  nm and a high surface area ( $> 50$  m<sup>2</sup>/g), provides a higher morphological  
15 selectivity and higher reactivity than heretofore attainable. The reactivity of these catalyst particles is maintained even after 24 hours reaction such that yield exceeds 200g carbon per gram of catalyst. The catalysts which are key to the products and yield achieved are  
20 prepared to specific parameters (size distribution, composition and crystallinity) specified and via a flame synthesis process as taught in U.S. Patent No. 6,132,653. The disclosure of U.S. Patent No. 6,132,653, is totally incorporated herein by reference thereto.

25 For purposes of this application the terms used herein will have the following definitions: "Purity" is defined as carbon content with the impurity understood to comprise the catalyst.

"Selectivity" is defined as fraction of the  
30 carbonaceous product possessing the intended morphology (orientation of graphene layers); and "yield" is defined as weight carbon produced divided by weight of catalysts; in such catalytic processes, this is also sometimes expressed as turnover.

35 Therefore, it is a principal object of the present

invention to synthesize a pure carbon nanomaterial with extremely high purity, high selectivity, of the carbon morphology and exceptionally high yield.

5 It is a further object of the present invention to synthesize a pure carbon nanomaterial in the presence of a custom made catalyst having a particular particle size, surface area, and chemical composition to provide the high morphological selectivity, yield, and purity.

10 It is a further object of the present invention to produce a carbon nanomaterial in the presence of a custom made catalyst so that over a given amount of time the yield exceeds 200gcarbon/g of catalyst.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 For a further understanding of the nature, objects, and advantages of the present invention, reference should be had to the following detailed description, read in conjunction with the following drawings, wherein like reference numerals denote like elements and wherein:

20 Figure 1 is a graph of the Effect of Time on Growth of the carbon nanofiber in the presence of the Iron oxide catalyst over a 24 hour period;

Figure 2 is a graph of the Effect of Time on Growth of the carbon nanofiber in the presence of an Iron:Nickel catalyst over a 24 hour period;

25 Figure 3 illustrates the specific morphology of the carbon microstructure of the carbon nanofiber produced in the presence of the Iron oxide catalyst as described in relation to Figure 1;

30 Figure 4 is a high resolution view of the specific morphology of the carbon microstructure of the carbon nanofiber produced in the presence of the Iron oxide catalyst as described in relation to Figure 1.

35 Figure 5 illustrates the specific morphology of the carbon microstructure of the carbon nanofiber produced in the presence of the Iron:Nickel catalyst as described in

relation to Figure 2;

Figure 6 is a high resolution view of the specific morphology of the carbon microstructure of the carbon nanofiber produced in the presence of the Iron:Nickel catalyst as described in relation to Figure 2;

Figure 7 is a graph of the production of nanocarbon fibers having platelet morphology prepared with Iron oxide catalyst compared with a conventional catalyst; and

Figure 8 is a graph of the production of nanocarbon fibers having tubular morphology prepared with Iron:Nickel catalyst compared with a conventional catalyst.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS PROCESS FOR PRODUCING THE CATALYSTS

The production of the catalyst utilized in the production of the nanofibers disclosed herein is similar to that disclosed in U.S. Patent No.6,132,653, referenced and incorporated earlier herein.

List of metals that can be used as part of the catalyst are as follows:

Fe, Ni, Co, Mo, Cu, La, Ag, Au and alloys.

#### THE NANOCARBON MATERIALS PRODUCED WITH THE CATALYSTS

Reference is now made to the table and information below which discusses the properties of the material as produced with the new catalyst as described above (flame synthesized) and a conventional catalyst (co-precipitated).

"Table 2."

Properties	New Catalyst (flame synthesized)	Conventional or Commercial Catalyst (co-precipitation)
Chemical form	Metal Oxide	Pre-reduced Metal with thin cover of oxide
Size (nm)	~10	500-2000
Morphology	Single Crystal	Polycrystalline
Surface area (m <sup>2</sup> /g)	~ 130	<20
Packing density	Lower than bulk	Same as bulk

Experimental Detail to achieve results above:

10           a.   Conventional or commercial catalyst:

                  A known amount of pre-reduced catalyst (0.1g) was placed in a ceramic boat or a quartz cylinder. The boat was then transferred into a quartz reactor ( $\phi=47$  mm). The reactor was flushed for 30 min with nitrogen gas with a flow rate of 200sccm. The reactor was heated up to 450°C with a heating rate of 5°C/min under 10-20% H<sub>2</sub> (balanced with N<sub>2</sub>). This was held for 1 h at this temperature. The temperature was then increased to reaction temperature 600°C for iron or 650°C for iron-nickel catalyst in 30 min under N<sub>2</sub> flow. Once the set temperature was stabilized, the reaction gas (CO/H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>) was introduced into the reactor for different periods of time (1, 2, 4, 6, 8 and 24h).

25                   b.   New catalyst:

                  A known amount of oxide catalyst (0.1g) was placed in ceramic boat or a quartz cylinder. The boat was then transferred into the quartz reactor ( $\phi=47$  mm). The reactor was flushed for 30 min

with nitrogen gas with a flow rate of 200sccm. The reactor was heated up to 450°C with a heating rate of 5°C/min under 10-20% H<sub>2</sub> (balanced with N<sub>2</sub>). This was held for 1 h at this temperature than the temperature was increased to reaction temperature 550°C for iron oxide and iron-nickel oxide catalyst in 30 min under N<sub>2</sub> flow. Once the set temperature was stabilized, the reaction gas (CO/H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>) was introduced into the reactor for different periods of time (1, 2, 4, 6, 8 and 24h). The Iron oxide catalyst utilized with CO:H<sub>2</sub>::4::1 at 550°C produces a specific morphology of the carbon micro structure where the graphite planes are perpendicular to the carbon growth axis as seen in Figures 3 and 4. In comparison to the commercial catalyst, this trial shows a better carbon yield (2 to 3 time higher) and at 50°C lower synthesis temperature (550° vs 600°C). There is a greater than 99.6% purity of the carbon product which can be reached in the system. Morphological selectivity is 100%. In the second example, an Iron:Nickel catalyst was used, with C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>::1:4 at 550°C to produce a specific morphology of the carbon micro structure, i.e., where the graphite planes are parallel and/or at an angle to the carbon growth axis, as seen in Figures 5 and 6. In comparison to other conventional or commercial catalyst, this trial shows a better carbon yield(2 to 3 times higher) and at 100°C lower synthesis temperature (550° vs 650°C). A greater than 99.2% purity of the carbon product can be reached in this system. Morphological selectivity is >95%. In the two examples used above, the catalyst can be a metal

oxide catalyst selected from the metals including iron, nickel, cobalt, lanthanum, gold, silver, molybdenum, iron-nickel, iron-copper and their alloys.

5           c. Fluid Bed Process Option:

          A known amount of oxide catalyst (0.1-1.2g) was placed in a ebullated fluid-bed reactor with  $Al_2O_3$  (14.9-13.8 g). The reactor was flushed for 30 min with nitrogen gas with a flow rate of 1000sccm. The reactor was heated up to 450°C with a heating rate of 5°C/min under 10-20%  $H_2$  (balanced with  $N_2$ ). This was held for 1 h at this temperature then the temperature was increased to a reaction temperature 550°C for iron-nickel oxide catalyst in 30 min under  $N_2$  flow. Once the set temperature was stabilized, the reaction gas ( $C_2H_4/H_2$ ) was introduced into the reactor for a known period of time (2h). The yield can reach to 140g carbon/g catalyst.

          Reference is now made to Fig. 1 which shows the graph of the effect of time on growth of carbon nanofibers utilizing an iron oxide catalyst with  $CO:H_2::4:1$  at 550°C. In this graph, the carbon nanofibers produced comprise the carbon platelet morphology as seen in Figures 3 and 4. With reference to Fig. 1: As the process continues over some 24 hour period, the metal content as a percentage weight of the product decreases to 0.3% and the yield of carbon per gram of catalyst was >300g/g. It also shows that the catalytic particle was still active even after the 24 hours reaction time. In this particular example, the iron oxide catalyst, with  $CO:H_2::4:1$  at 550°C produced a specific morphology of the carbon micro structure, i.e., where the graphite planes are perpendicular to the carbon growth axis, again as depicted in Figures 3 and 4. Furthermore, in comparison to the commercial catalyst, as



stated earlier this trial shows a better carbon yield (2-3 times higher) and at 50°C lower synthesis temperature. This provides a 99.7 pure carbon product and with a morphological selectivity of 100%. As seen in Figs 3 and 4, the specific morphology of the carbon microstructure shows the graphite planes perpendicular to the carbon growth axis.

Turning now to Fig. 2, the graph depicts utilizing the iron-nickel catalyst with  $C_2H_2:H_2::1:4$  at 550°C. The carbon nanofibers which were produced as shown in this graph resulted in a specific morphology of the carbon microstructure, i.e., where the graphite planes are parallel or at an angle to the growth axis as seen in Figures 5 and 6. In comparison to the conventional catalyst, this shows a better carbon yield and at a 100°C lower synthesis temperature. Again there is a 99.6% purity of the carbon product and morphological selectivity is >95%. At the end of a 24 hour reaction period, the metal content of the product was 0.4% while the yield of carbon was between 200 and 250g/g catalyst.

In both of these systems, as shown in Figs. 1 and 2, there can be reached a 99% carbon in an 8 hour reaction time. These results are shown in the following tables.

In each of these tables and as depicted in Figures 7 and 8 respectively, both the Iron catalyst and the Iron:Nickel catalyst respectively produced a carbon nanomaterial platelet or tubular morphology at lower temperature, >95% morphological selectivity, higher yield and lower impurity of metal than the commercial or conventional catalysts.

For Platelet morphology, catalyst Iron, CO:H<sub>2</sub>::4:1.

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Catalyst	Temperature (°C)	Selectivity (visual)	Yield (g/6h)	Impurity (metal)
Flame	550	100	77	1.3
Commercial (J.T. Baker)	600	90	50	2

For Tubular morphology, catalyst iron:nickel::8:2, C<sub>2</sub>H<sub>4</sub>:H<sub>2</sub>::1:4

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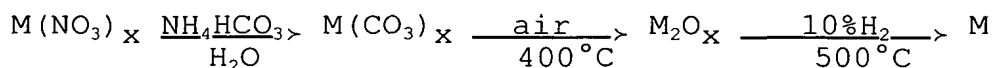
Catalyst	Temperature (°C)	Selectivity (visual)	Yield (g/6h)	Impurity (metal)
Flame	550	>95	81	1.25
CCC Produced Conventional	650	60	26.33	3.8

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The "CCC Produced Conventional" catalyst was prepared utilizing a liquid precipitation process. Iron, nickel, and copper metal nitrates were utilized. The metal nitrates were stoichiometrically mixed in H<sub>2</sub>O and rapidly stirred at room temperature. Ammonium bicarbonate is added to a pH ~9, and stirred ~5 minutes. A precipitate forms overnight; the precipitate is washed and dried. Metal carbonate is dried at 110°C for 24 hrs. and then calcinated in air for 4 hrs. at 400°C. Metal oxides are ball milled for 6 hrs. and reduced in 10% H<sub>2</sub> in N<sub>2</sub> at 500°C for 20 hrs. in 200 sccm flow. Metal powder is passivated in 2% O<sub>2</sub> in N<sub>2</sub> at room temperature for 1 hour. This technique and the reaction taking place, as shown below, are referenced in R.J. Best and W.W. Russel, J. Am. Chem. Soc. 76, 8383 (1954).



#### Powder catalyst Synthesis by Flame/Plasma process:

A mixture of nitrate/sulfate salt of metal (Fe, Ni and Cu) ethanolic solution were prepared and vaporized/atomized into either flame or plasma torch and powder of pure oxide or mixed metal oxide were obtained by this process. US patent 6,123,653 (Oct 17, 2000).

In general, the process for producing nanocarbon materials, is undertaken by providing a catalyst with an average particle size of  $\leq 10$  nm and a surface area greater than 50 m<sup>2</sup>/g, although this may vary. Next, carbonaceous reactants are reacted in the presence of the catalyst over a given period of time to produce carbon nanofibers with over 99% purity and a morphological selectivity approaching 100% with higher reactivity.

The catalyst, produced by the method described in U.S. Patent No. 6,123,653, incorporated herein by reference, is a metal oxide catalyst selected from the metals including iron, nickel, cobalt, lanthanum, gold, silver, molybdenum, iron-nickel, iron-copper and their alloys.. There may be other suitable metal oxides which may be found as experimentation continues. The catalyst, itself, is prepared to specific parameters (size distribution, composition and crystallinity) specified and via a flame synthesis process; and it possesses a single crystal morphology. By utilizing the catalyst from the group identified, the resulting yield of carbon nanomaterial is  $\geq 140$ g carbon per g catalyst, but it may be more, while the morphology of the carbon micro structure comprises graphite planes of controllable orientation (depending on catalyst composition and carbonaceous feedstock) perpendicular or parallel to the carbon growth axis resulting in the 99.6% purity of the carbon product.

The foregoing embodiments are presented by way of example only; the scope of the present invention is to be

limited only by the following claims.